Characteristics of element concentration of daytime and nighttime $PM_{2.5}$ in the suburbs of Shanghai using Synchrotron XRF*

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Abstract The characteristics of daytime and nighttime suburbs $PM_{2.5}$ in Shanghai were analyzed by synchrotron based X-ray fluorescence during the period of October, 2006 and November, 2007. The mass concentrations of nighttime $PM_{2.5}$ was approximately two times that of daytime $PM_{2.5}$. Some elements, such as Zn, Cu, Mn, Cl were found enriched at night. The local sources might have significant contribution to the nighttime $PM_{2.5}$ pollutions.

Key words $PM_{2.5}$, mass concentration, elements concentration, synchrotron X-ray fluorescence

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1 Introduction

Recent epidemiological studies revealed that increasing atmospheric particulate matters pollution might induce respiratory symptoms, hospitalization and cardiovascular diseases in humans[1]. Fine particles ($PM_{2.5}$) are particularly hazardous to human health because they can reach deep respiratory tracts and contain/absorb more toxic substances due to small size. Therefore, $PM_{2.5}$ attracts much attention all over the world. In China, the average mass concentration of many big/mega-cities such as Beijing[2], Shanghai[3, 4] and Nanjing[5] is much higher than EPA $PM_{2.5}$ limitation 65 μg/m^3. Metals are important trace substances of atmospheric particulate matters not only due to their toxicity but also duo to the ability to track specific emission sources. Yang Fumo[6] compared the characteristics of metal distribution in $PM_{2.5}$ in Beijing and Shanghai to analyze the influence of dust storm. Yue Wei-sheng tracked the emission sources of $PM_{2.5}$ in Shanghai by elements distribution in single particles[7, 8]. The air pollution in urban area has drawn much attention all over the world. However, atmospheric pollution of suburb and rural areas has not attracted enough attention till now[9].

The mass concentration variation is one of the most important properties of atmospheric particle pullution. Tan Rong-hua[4] and Wang Jing-li[10] studied the time-dependence of mass concentration in Shanghai and Beijing, and the results revealed that the mass concentration varies dramatically in different time. It might be influenced by many aspects such as meteorological conditions, locale emissions and long-distance transportation.

In this paper, the mass concentration and elements distribution in $PM_{2.5}$ of daytime and nighttime are concerned. Synchrotron Radiation XRF is introduced to measure the trace elements in $PM_{2.5}$. The results are expected to be useful for tracing the emission sources of nighttime pollution.

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2 Experimental

2.1 Sampling

The study area was in Jiading District, a suburb of Shanghai, about 15—20 km away North-east of Wusong Industrial Estate. The sampling site was located in a building roof of Shanghai Institute of Applied Physics (31°24′N, 121°17′E), about 18 meters above the ground level without high buildings nearby.

The $PM_{2.5}$ samples were collected using median volume sampler $PM_{10}/PM_{2.5}$-2 at the flow rate of 70 L/min. The samples were collected on Oct. 15, 2006, Feb. 5, Feb. 9 and Feb. 9, 2007. The sampling periods of daytime and nighttime were 8:00∼20:00 and 20:00∼8:00, respectively. Millipore Cellulose filters were used as collection substrates with the diameter of 90 mm. The mass concentrations of particulate matters were obtained by weighting the filters before and after sampling.

ELPI (Electrical Low Pressure Impactor, DEKATI Corp.) was used to monitor the variation of mass concentration in 24 hours. ELPI can collect particulate matters in 13 sizes smaller than 10 μm and register the real-time mass concentration and particle number concentration simultaneously[11, 12].

2.2 Analysis

Synchrotron X-ray fluorescence spectra were obtained at the XRF Station (4W1B) of Beijing Synchrotron Radiation Facility (BSRF). The electron energy and maximum ring current of BSRF storage ring were 2.5 GeV and 160 mA, respectively. The beam was monochromatized at about 15 keV by a multilayer monochromator, and then focused by a K-B mirror with the spot size of 20×30 μm. A Si(Li) detector with energy resolution of 133 eV (at 5.9 keV) was placed at 90° to the incident-beam direction. Each sample was measured in air for 300 seconds. QXAS was used to analyze the XRF spectra[13].

3 Results and discussion

3.1 Mass concentrations

Mass concentration of $PM_{2.5}$ of daytime and nighttime during Oct. 15, 2006 and Mar. 9, 2007 was shown in Fig. 1. The mass concentrations of autumn and winter (October and December) were obviously higher than spring (February and March). It corresponded with the results of seasonal $PM_{2.5}$ mass concentration variation of Shanghai studied by Chen Ming-hua[3]. In the meantime, the mass concentration of nighttime was much higher than daytime.

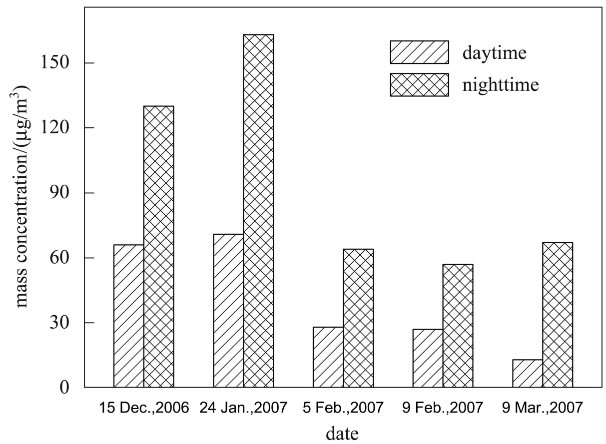

Fig. 1. Mass concentration of $PM_{2.5}$ of Daytime and Nighttime.

To reveal the variation of $PM_{2.5}$, an ELPI was used to record the detailed variation of $PM_{2.5}$ mass concentration continuously within 24 hours, as shown in Fig. 2. The mass concentration increased dramatically around 18:00 and decreased suddenly around 8:00. The maximum mass concentration appeared after midnight. The average mass concentrations of daytime and nighttime are 0.32 mg/m^3 and 0.50 mg/m^3, respectively. It is consistent with the results by gravimetric method.

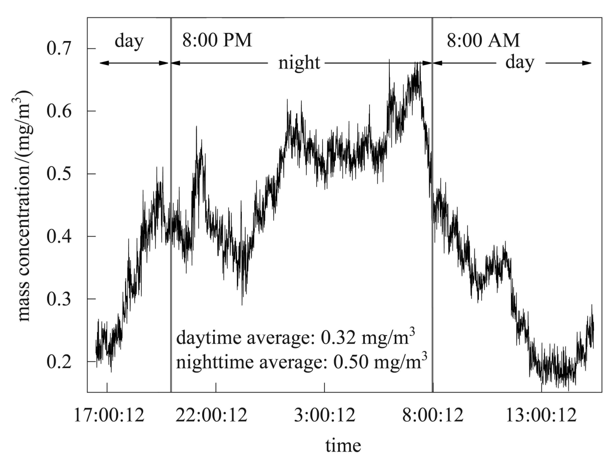

Fig. 2. Mass concentration variation of PM less than 2.4 μm ($PM_{2.4}$) in 24 hours, from Nov. 3 to 4, 2007.

However, the characteristics of mass concentration variation are slightly different from other reports[4, 10, 14]. In these studies, the maximum mass concentrations exhibited two peaks at 6:00∼9:00 and 18:00∼20:00, respectively. The high mass concentration between 18:00∼20:00 was due to bad diffusion condition induced by lower temperature. After midnight, the mass concentration decreased because of diffusion process. But in this paper, the mass concentration increased after midnight. It implies that not only the meteorological conditions but also the nighttime emissions might contribute to fine particulate matters at night.

3.2 Element concentrations

The element distribution is also an important aspect of particulate matters and can be used to track the features of pollution sources. Due to the decreasing current in the storage ring, the counts of XRF spectra should be normalized according to the incident photo strength detected by a pre-ionization chamber[15]. Fig. 3 shows the XRF spectra (already normalized) of Feb. 5 and Feb. 9, respectively. It is obvious that several elements such as Cl, Ni, Cu, Zn are more concentrated at night.

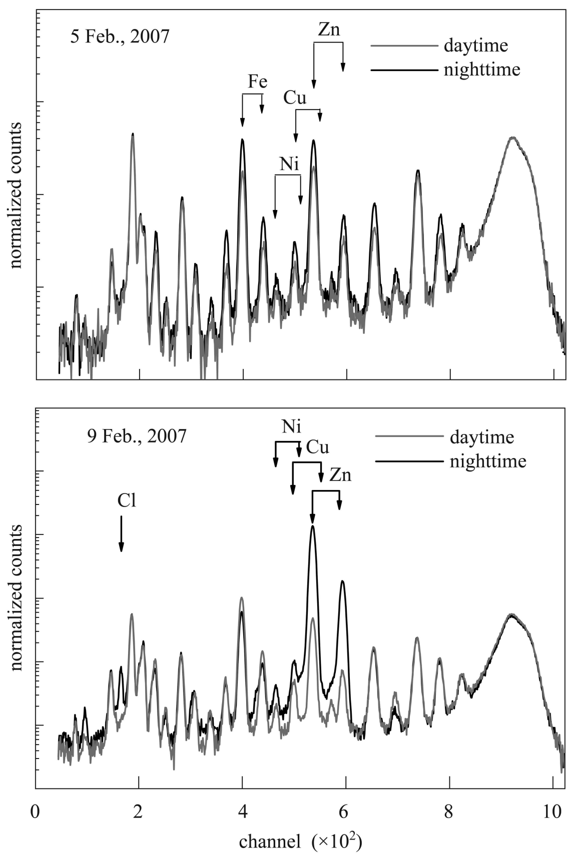

Fig. 3. Normalized XRF spectra of Feb. 5 and Feb. 9, 2007.

In order to compare the relative concentration of each element, the peaks of each element was calibrated by sampling air volume as shown in following equation:

$$M_i = \alpha \cdot \frac{A_i}{V} \cdot \frac{C_i^{\rm s}}{A_i^{\rm s}}, \tag{1}$$

where i presents the element, M_i is the relative concentration of element i, A_i and $A_i^{\rm s}$ are the normalized peak areas of element i in samples and reference material, respectively, V is the sampling volume, $C_i^{\rm s}$ is the concentration of element i in standards, α is the coefficient related to geometric condition such as solid angle of detector. NIST No. 2 was used as the reference material in this study.

The relative concentrations of elements in $PM_{2.5}$ are listed in Table 1. It can be concluded that some elements (Zn, Mn, Cu, et al) are more concentrated at night, especially Zn.

Table 1. Relative concentrations of elements in $PM_{2.5}$ (arb.uni./m^3).

elements	Feb. 5		Feb. 9	
	day	night	day	night
K	39.2	43.7	28.5	33.6
Ca	29.7	42.4	18.6	12.7
Ti	12.8	14.9	2.8	3.0
Mn	1.8	4.9	0.8	0.7
Fe	18.7	40.8	14.9	9.0
Ni	0.8	1.2	0.3	0.7
Cu	0.8	1.6	0.4	0.9
Zn	13.7	25.4	4.3	137.6
Br	0.2	0.2	0.1	0.1
Pb	3.0	5.4	1.5	1.4

Zn, Mn, Cu, Cl are the typical emission elements of anthropogenic sources[16]. However, the influence of industrial estate should be quite uniform in the sampling site in spite of daytime or nighttime since it is 15—20 km away. Since the sampling site is surrounded by some public boilers, industrial kiln stoves and irregular solid waste incineration, these emission sources may contribute much in Mn, Zn, et al.[17].

All these evidences indicate that local emission sources may be active at night, and the characteristics of pollutants of nighttime need further study.

4 Conclusions

The mass concentration and element concentration of daytime and nighttime $PM_{2.5}$ are studied in this paper. The results indicate that the average mass concentration of nighttime is twice that of daytime. Some elements (Zn, Mn, Cu, et al) are more enriched at night. Based on these evidences, it can be concluded that local anthropogenic sources are more active at night.

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References

1 Dockery D W, Schwardz J. Inhalation Toxicology, 1995, **7**: 1—18

2 HAO M T, LIN T J, LIU Y. Environ. Sci. Manag., 2006, **31**: 58—61 (in Chinese)

3 CHEN M, LI D, CHEN C H. Shanghai Environmental Science, 2003, **22**: 1038—1041 (in Chinese)

4 TAN R H, ZHANG Y M, ZHENG S F et al. J. Environ. Occp. Med., 2004, **21**: 226—229 (in Chinese)

5 CONG J, WU X, RU D F et al. Jiangsu Environ. Sci. Technol., 2006, **19**: 46—48 (in Chinese)

6 YANG FM, YE B M, HE K B et al. Sci. Total Environ., 2005, **343**: 221—230

7 YUE W S, LI Y, LI X L et al. J. Synchron. Rad., 2004, **11**: 426—431

8 YUE W S, LI X L, LIU J F et al. Sci. Total Environ., 2006, **368**: 916—925

9 ZHOU Z F, LIU K, SUN Y L. Research of Environ. Sci., 2006, **19**: 24—28 (in Chinese)

10 WANG J L, XIE Z, ZHANG Y H et al. Acta Meteorologica Sinica, 2004, **62**: 105—111 (in Chinese)

11 Keskinen J, Pietarinen K, Lehtimäki. J. Aerosol Sci., 1992, **23**: 353—360

12 Marjamäki M, Keskinen J, CHEN D R et al. J. Aerosol Sci., 2000, **31**: 249—261

13 Win QXAS, IAEA Laboratories, Seibersforf (Austrialia), Version 1.3., 1997-2001, http://www.iaea.or.at/programmes/ripc/physics/faznic/winqxas.htm

14 YU J H, YU T, WEI H et al. Research of Environ. Sci., 2004, **17**: 45—47 (in Chinese)

15 YAO H Y. Synchrotron X-ray analysis. In: Application of Synchrotron Radiation, 2005, 373

16 Stigter J B, De Haan H P M, Guicherit R et al. Environ. Pollut., 2000, **107**: 451—464

17 LI R D, NIE Y F, WANG L et al. China Environmental Science, 2004, **24**: 480—483 (in Chinese)